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QUALITY AND APPLICATIONS OF ASPHALT DERIVED FROM UPGRADED HEAVY CRUDE

FINAL REPORT

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QUALITY AND APPLICATION OF ASPHALT PRODUCED FROM UPGRADED COLD LAKE BITUMEN

M.A. Poirier

SUMMARY

In this work, we have examined the potential for utilizing the residual bottoms fraction remaining after upgrading heavy Canadian crude, as a source of asphalt. Feed samples from Visbreaking and RESIDFINING processes have been investigated. The results have shown that the upgraded residues alone are not suitable for road applications. However, blending of those residues with conventional Cold Lake asphalt allows the preparation of paving and roofing asphalts that meet specifications for the intended use.

SOMMAIRE

Dans cette étude nous avons examiné la possibilité d'utiliser des fractions résiduelles produites par valorisation de bruts canadien pour la préparation de bitumes. Des produits provenant des procédés de viscoréduction et RESIDFINING ont été étudiés. Les résultats démontrent que les résidus de valorisation ne rencontrent pas les normes pour les bitumes routiers. Cependant, le mélange de ces résidus de valorisation avec le bitume de Cold Lake conventionel permet d'obtenir des bitumes routiers et de toîture qui recontrent les normes pour l'application désirée.

1. INTRODUCTION

Most of the conventional asphalts produced by refineries are obtained from straight run distillation of crude oil. However, refiners are now looking to upgrade heavy crudes or distillation residues in order to produce more transportation fuels. These upgrading processes could also be used as a tool for viscosity reduction of heavy oils or bitumens to obtain pipelineability.

Presently, refiners who have upgraders dispose of residual material as fuel. However, incorporation into asphalt would realize a higher market value for these residues.

Studies of thermally cracked asphalts have been the subject of many publications(1-4). It has been reported that thermally cracked asphalts have poor low temperature properties, poor ageing properties, and do not meet viscosity requirements(1,5). However, asphalt prepared by mixing visbroken residue (510°C+) with 200/300 penetration Athabasca asphalt has been shown to have good characteristics(3).

In this study, 85/100 penetration residues from Visbreaking and RESIDFINING Cold Lake bottoms and blended asphalts obtained by mixing virgin Cold Lake asphalt with them were examined. Our goal was to prepare 85/100 penetration asphalts that would meet Canadian specifications.

2. DISTILLATION AND BLENDING OF THE SAMPLES

The distillation cut point and yield versus penetration of the residues from Visbreaking, and RESIDFINING Cold Lake bitumen are represented in Figures 1 and 2. The results indicate that, for a given penetration, conversion processing decreases the yield of residue. The yield and cut point are affected by the nature of the process and the degree of conversion. For example, less asphalt of a given penetration grade would be produced from RESIDFINING than from Visbreaking Cold Lake crude (Figure 2).

In this study, conversion residues and blends containing 25 and 50 wt% conversion residue were evaluated as paving asphalt. The properties of the conversion residues and blends of 85/100 penetration residues from Visbreaking, and RESIDFINING Cold Lake bitumen with 85/100 Cold Lake vacuum residue were determined. One asphalt made by blending 510°C+ residue from Visbreaking process with 300/400 penetration Cold Lake vacuum residue was also studied.

3. PAVING ASPHALT SPECIFICATIONS

Asphalts have a complex rheological behaviour and have to meet narrow specifications. The asphalt cement specifications vary from one province to another in Canada, and are different from one country to another. The specifications for 85/100 penetration asphalt cements for some provinces in Canada are presented in Table 1. The most critical property is the viscosity vs penetration relationship. Figures 3 to 6 illustrate the viscosity specifications at 135°C for Ontario, Alberta and New Brunswick as well as the proposed new Canadian Government Standards Board (CGSB) specifications. It can be seen that Alberta has the most restrictive specifications while New Brunswick has the least restrictive. Nova Scotia, Newfoundland and British Columbia have no viscosity specifications at 135°C, however, British Columbia has a viscosity limit at 60°C which requires asphalt quality similar to that in New Brunswick. Alberta, Saskatchewan and Manitoba do not use 85/100 penetration asphalt. The minimum viscosity limits for their 150/200 and softer grades are similar to those of the proposed CGSB specifications.

The critical specifications for products containing conversion residues are the high temperature viscosity, resistance to hardening as indicated by the Thin Film Oven Test (TFOT) and solubility in trichloroethylene, because these are properties which are most likely to be degraded by the conversion processes.

4. PROPERTIES OF THE ASPHALTS

4.1 Conversion Residues Compared to Cold Lake Vacuum Residue

The physical properties of 85/100 penetration Cold Lake residue and 85/100 penetration residues from Visbreaking, and RESIDFINING Cold Lake asphalts are presented in Table 2.

RESIDFINING residue (Sample 2) meets most of the specifications except for the ductility of the TFOT residue, which was found to be the lowest of all samples (8 cm), and far below the minimum required by some provinces (100 cm minimum). The viscosity ratio of 3.11 at 60°C is within usual specification limit of 4 maximum and the percentage of retained penetration is high. However, a skin formed on the surface during the TFOT, and this probably inhibited oxidation of the asphalt, resulting in less than expected hardening.

The Visbroken residue (Sample 5) does not meet the viscosity requirements at 135°C in Ontario and Quebec (Figure 3). The minimum viscosity for 85/100 penetration asphalt in these provinces is 280 cSt. However, this residue would meet the minimum viscosity requirements for 85/100 penetration asphalt in the Maritime provinces and British Columbia. Visbroken residue does not have acceptable retained penetration on the TFOT residue and the increase in viscosity is too high. The value of 46.5% is borderline to the minimum value of 47% required by several provinces, and below British Columbia's minimum limit of 55%.

Inspection of the solubility in trichloroethylene results show that all the processed Cold Lake asphalts (Samples 2, 5) have high solubility. This indicates that there is no coke formed from upgrading Cold Lake by these processes at the conversion levels used.

4.2 Blends of Conversion Residues with Cold Lake Vacuum Residue

The physical properties of the blends evaluated are presented in Table 2. All the blends meet the specifications for 85/100 penetration asphalt. Moreover, some properties of the blends are improved compared to Cold Lake asphalt (Sample 1).

Cold Lake asphalt is a volatile asphalt, as shown by its relatively low flash point. The flash point of the blends (Samples 3, 4, 6, 7) is higher by 8 to 46°C. The volatility of the blends in the Thin Film Oven Test is also less than for Cold Lake vacuum residue. However, blends made with 300/400 penetration Cold Lake residue has relatively high volatility, due to the high volatility of the 300/400 penetration Cold Lake asphalt component.

The viscosity at 135°C of the blends are all above 280 cSt minimum requirement in Ontario and Quebec. However, the blend containing 50% Visbroken residue is borderline with the minimum requirement for the 85/100 penetration. Meeting of the viscosity specification could only be obtained from blending with a non-processed asphalt of higher viscosity such as Cold Lake.

The results in Table 2 indicate that at least 50 wt% of RESIDFINED or Visbroken 85/100 penetration asphalt could be blended with Cold Lake asphalt of same penetration grade.

By calculating the Pen-Vis Number (PVN)(6) for the asphalts, it is possible to predict if the corresponding 150/200 penetration grade asphalt cements would meet the viscosity requirements in the different provinces. The results are illustrated in Figures 3 to 5. In order to make 150/200 penetration asphalt cement in Ontario, Quebec and prairie regions, it would be necessary to have a PVN $\geq$-0.50. Therefore, blend containing even 25% Visbroken residue would not be acceptable as 150/200 penetration asphalt cement in these provinces. Blends containing 50% of these conversion residues would pass the viscosity specifications for 150/200 penetration asphalt in the Maritime provinces.

5. TEMPERATURE SUSCEPTIBILITY

The temperature susceptibility of asphalt cements at temperatures below 25°C is not part of the specifications in North America, but is one of the most important properties for predicting the behaviour of asphalt pavements when subjected to thermal stresses. Temperature susceptibility of an asphalt cement is the variation in consistency (viscosity or penetration) as a function of the temperature. Asphalt cement with low temperature susceptibility (higher PI) is the most desirable because it has resistance to low temperature pavement cracking and high temperature rutting of pavements during summer.

There is no standard procedure for the determination of the Penetration Index. The method that we have used has some similarities with the method developed by the Laboratoire des Ponts et Chaussees (LCPC) in France(7). The method used consisted of determining the penetration of the asphalt cement at 4°, 10°, 25° and 30°C. The slope of the best straight line representing these data is obtained from a plot of $\log_{10}$(penetration) vs temperature. The Penetration Index (PI) is calculated from the following equation:

$$PI = \frac{20 - 500A}{50A + 1}$$

where

$$A = \frac{d \log_{10}(Pen)}{dT}$$

This method gives results similar to the standard EPC method which uses penetration measurements at 25°C, 10°C and 4°C.

The Penetration Indices of the asphalt samples prepared in this work are presented in Table 2. All the conversion residues and blends have as high or higher PI than Cold Lake asphalt (Sample 1). For most of the road asphalts on the market in North America, the PI ranges from about -0.5 to -1.5. Asphalt having a PI in that range would be considered to be moderately temperature susceptible. REDEFINED residue with a PI of +1.22 has very low temperature susceptibility, and blending it with Cold Lake asphalt results in higher PI than that of the vacuum residue. This is also observed to a lesser extent with the Visbroken residue.

6. COMPOUND-TYPE DISTRIBUTION

The chemical composition of an asphalt is important because it controls the rheological behaviour. The asphalts investigated in this work were separated into saturates, naphthene-aromatics, polar aromatics and asphaltenes using ASTM procedure D 4124. The separation scheme is illustrated in Figure 7. The asphaltenes were first precipitated with n-heptane. The malthenes (n-heptane solubles) were then submitted to a chromatographic separation on calcined alumina. The saturates were eluted from the alumina column with n-heptane. The naphthene-aromatics were eluted with toluene and

the polar aromatics were recovered with a 50/50 methanol-toluene solvent mixture followed by trichloroethylene and finally methanol, which improves the recovery of the polar aromatics. In all cases, the recovery was higher than 98%. The chemical composition of the different samples is presented in Table 3.

The saturates content was about the same for the conversion residues and blends as compared to Cold Lake asphalt (Sample 1). However, the conversion processes resulted in increased the naphthene-aromatics content at the expense of the polar aromatics content (Samples 2, 5). The asphaltenes content was about the same for all samples except for RESIDFINED residue (Sample 2) and the corresponding blends (Samples 3, 4) which was slightly lower and for the visbroken residue (Sample 5) which had significantly higher asphaltenes content at 24.1%.

Asphaltenes have a very complex structure which results from the presence of high molecular weight compounds and association through hydrogen bounding of polar aromatic compounds. Therefore, combination of two different blending components with different asphaltenes content will not necessarily result in a mixture with the average asphaltenes content. Re-association of the polar aromatics fractions of the two components will be undoubtedly different. This explains why the asphaltenes content for blends of Cold Lake residue with RESIDFINED residue are lower than expected.

An asphalt with high asphaltenes content does not necessarily have high viscosity. The Visbroken residue (Sample 5) has the highest asphaltenes content and the lowest viscosity (Table 3). In general, the asphaltenes content is affected by the nature of the conversion process and the level of conversion.

The results in Table 3 also show that for a given asphaltenes content, the PI is improved by the presence of naphthene-aromatics while the polar-aromatics make the temperature susceptibility poorer(8). Thus, it is possible to correlate the rheological behaviour with the composition of asphalts.

The colloidal structure of asphalts can be classified by the Colloidal Instability Index (I_C) which is a function of the composition.

$$I_C = \frac{\text{Asphaltenes + Saturates}}{\text{Naphthene-aromatics + Polar aromatics}}$$

An asphalt with an $I_C > 0.5$ is referred as a "gel" type while an asphalt with $I_C < 0.5$ is referred as a "sol" type. According to this definition, all the asphalts prepared in this work are "sol" type except the Visbroken residue (Sample 5) which is marginally a "gel" type with $I_C = 0.53$.

Although the chemical composition of asphalt governs the rheological properties, I_C is not useful for characterizing rheological behaviour. Two asphalts may have same I_C but different composition (Samples 2, 3) and different rheological properties (Table 2).

7. SIMULATED AGEING OF ASPHALTS BY RTFOT

It is important to know what will happen to asphalt during mixing with aggregates. In order to study hardening of non-conventional asphalts, we have used the Rolling Thin Film Oven Test (RTFOT). This standard test (ASTM D 2872) simulates the types of changes in asphalt that occur during hot-mix preparation. It consists of oxidizing at 163°C a moving thin film (about 2 mm) of asphalt under an air flow rate of 4 ℓ/min. for 75 minutes.

Ageing of asphalt is caused primarily by oxidation with air, a process which is more favoured at high temperatures and thin asphalt films such as occur when asphalt is mixed with hot aggregates. During oxidation, the naphthene-aromatics are converted to polar aromatics and the latter to asphaltenes. This results in an increase in viscosity and asphaltene content as shown in Table 4.

Comparison of the viscosities on the residue and viscosity ratios at 60°C shows that the RTFOT is more severe for the non-conventional asphalts. However, in the case of Cold Lake residue (Sample 1), both tests seem to have about the same severity.

In order to study the rheological behaviour of these asphalts during ageing, we have chosen the cone and plate viscometer which allows us to monitor the viscosity as a function of the shear rate.

The relative low viscosity increase in the TFOT compared to that in the RTFOT of the RESIDFINED residue is due to the formation of a skin on the surface of the sample during exposure in the Thin Film Oven. This skin, which would reduce the extent of oxidation during the exposure, was removed before testing the residue.

The cone and plate curves of the viscosity vs shear rate for these asphalts are presented in Figures 8 to 14. All asphalt samples show Newtonian behaviour except RESIDFINED 85/100. The high viscosity ratio (Table 4) and low ductility of the TFOT residue (Table 2) are consistent with this behaviour.

8. CONCLUSIONS

The quality of paving asphalts produced from Visbroken and RESIDFINED Cold Lake residues as well as 25/75 and 50/50 cracked asphalt/Cold Lake asphalt blend mixtures has been evaluated. The results show that Visbroken and RESIDFINED Cold Lake residues are not marketable as road asphalt as they don't meet highway department

specifications. However, blending of these upgrader residues with Cold Lake vacuum reduced asphalt resulted in improvement of their unsatisfactory characteristics.

RESIDFINED residue has the best characteristics for use as blending component for paving asphalt, followed by Visbroken residue.

The rheological properties of the blends of conversion residues with Cold Lake vacuum residue, as indicated by their Penetration Indices were found as good as those commercial asphalt cements. However, the viscosities at 135°C of some mixtures were below the minimum requirements of provincial asphalt cement specifications. Blends containing up to 50 wt% RESIDFINED residue or 25 wt% Visbroken residue would pass the most restrictive Canadian paving asphalt specifications.

9. REFERENCES

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10. TABLES

TABLE 1

85/100 ASPHALT CEMENT SPECIFICATIONS IN SOME PROVINCES IN CANADA

Penetration Grade	Ontario and Quebec 85/100		British Columbia AC-8		New Brunswick 85/100		Nova Scotia 85/100		Alberta 150/200 (A)	
	min	max	min	max	min	max	min	max	min	max
Requirements										
Flash Point (COC), °C	232	-	235	-	232	-	230	-	205	-
Pen 25°C, 100g, 5s	85	100	80	-	85	100	85	100	150	200
Viscosity, 135°C, cSt	280	-	-	-	170	-	-	-	255	360 at 150 pen
60°C, Pa.s	-	-	65	95					205	285 at 200 pen
									78	155 at 150 pen
									50	92 at 200 pen
Ductility										
4°C (1 cm/min)	6	-	-	-	-	-	-	-		
25°C (5 cm/min)	-	-	100	-	100	-	100	-	100	-
Thin Film Oven Test (5 h, 163°C)										
Change in Mass, %	-	-0.85	-	-	-	-0.85	-	-	-	-
Residue:										
Retained Pen at 25°C, %	47	-	55	-	47	-	47	-	-	-
Viscosity Ratio at 60°C									-	4.0
Ductility at 25°C	75	-	-	-	-	-	-	-	-	-
Solubility in Trichloroethylene, %	99.5	-	99.0	-	99.5	-	99.0	-	99.5	-

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TABLE 2

PHYSICAL PROPERTIES OF 85/100 CONVERSION RESIDUES AND BLENDS WITH 85/100 COLD LAKE

Composition, wt%								
RESIDFINED 85/100	–	100	50	25	–	–	–	
Visbroken 85/100	–	–	–	–	100	50	25	
Vacuum Reduced 85/100	100	–	50	75	–	50	75	(1)
Sample	1	2	3	4	5	6	7	11
Softening Point, °C (D36)	43.7	48.0	44.2	43.3	42.8	42.6	43.0	44.0
Flash Point, °C (COC)	278	366	324	308	290	288	286	292
Penetration								
30°C, 100g, 5s	150	127	147	145	139	142	148	163
25°C, 100g, 5s	89	91	92	92	86	87	88	97
10°C, 100g, 5s	17	29	23	20	19	19	18	22
4°C, 100g, 5s	9	18	10	9	10	10	9	11
Penetration Index (PI)	-1.09	+1.22	-0.36	-0.82	-0.67	-0.68	-0.91	-0.65
PVN	-0.37	-0.08	-0.27	-0.33	-1.29	-0.78	-0.55	-0.51
Viscosity, 60°C, Poises	1911	3438	2000	1939	1517	1693	1835	1754
100°C, cSt	3146	4483	3218	3238	1926	2528	2951	2850
135°C, cSt	396	473	414	398	220	306	354	338
Ductility at 4°C, (1 cm/min)	34	9.0	17	25	14	38	42	15.5
at 25°C (5 cm/min)	>150	>150	>150	>150	>150	>150	>150	>150
Solubility in Trichloroethylene, %	99.99	99.99	99.98	99.98	99.94	99.95	99.97	99.95
Thin Film Oven Test								
Change in Mass, %	-0.19	+0.07	-0.04	-0.10	-0.21	-0.17	-0.16	-0.86
Retained Pen at 25°C, %	58.4	78.2	66.5	65.2	46.5	58.0	64.0	55.1
Viscosity at 60°C, Poises	5431	10,680	5347	4654	8737	5079	4642	5330
Viscosity Ratio at 60°C	2.84	3.11	2.67	2.40	5.76	3.00	2.53	3.04
Ductility at 25°C (5 cm/min)	>150	8.0	>150	>150	>150	>150	>150	>150

(1) 26 wt% Visbroken (510°C+)/74 wt% Cold Lake 300/400 Pen.

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TABLE 3

CHEMICAL COMPOSITION OF ASPHALTS AND ASPHALT BLENDS, WT%
(ASTM D 4124)

Composition, wt%(1)								
RESIDFINED 85/100	-	100	50	25	-	-	-	
Visbroken 85/100	-	-	-	-	100	50	25	
Vacuum Reduced 85/100	100	-	50	75	-	50	75	(2)
Sample	1	2	3	4	5	6	7	11
Saturates	9.9	10.6	10.9	10.8	10.5	10.3	9.8	10.9
Naphthene-Aromatics	33.9	47.0	40.0	38.3	37.8	37.2	37.2	35.4
Polar Aromatics	36.7	25.3	32.3	34.0	27.6	30.7	33.3	34.2
Asphaltenes	19.5	17.1	16.8	16.9	24.1	21.8	19.7	19.5
I_C(4)	0.41	0.38	0.38	0.38	0.53	0.47	0.42	0.44
PI	-1.09	+1.22	-0.36	-0.82	-0.67	-0.68	-0.91	-0.65
PVN	-0.37	-0.08	-0.27	-0.33	-1.29	-0.78	-0.55	-0.51

(1) Normalized to 100%.
(2) 26 wt% Visbroken (510°C+)/74 wt% Cold Lake 300/400 Pen.
(3) I_C = Colloidal Index = $\frac{\text{Asphaltenes + Saturates}}{\text{Naphthene-Aromatics + Polar Aromatics}}$

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TABLE 4

AGEING PROPERTIES OF ASPHALTS (TFOT/RTFOT)(1)

Composition, wt%							
RESIDFINED 85/100	-	100	50	25	-	-	-
Visbroken 85/100	-	-	-	-	100	50	25
Vacuum Reduced 85/100	100	-	50	75	-	50	75
Sample	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Penetration at 25°C (100/5)							
Original	89	91	92	92	86	87	88
TFOT	52	71	61	60	40	51	56
RTFOT	53	59	52	52	37	45	49
Change in Mass, %							
TFOT	-0.19	+0.07	-0.04	-0.10	-0.21	-0.17	-0.16
RTFOT	-0.18	+0.08	-0.02	-0.06	-0.19	-0.10	-0.09
Asphaltenes, wt%							
Original	19.5	17.1	16.8	16.9	24.1	21.8	19.7
TFOT	20.2	18.7	16.2	19.7	25.8	22.0	21.0
RTFOT	20.6	18.3	19.3	19.9	25.5	23.7	21.5
Viscosity, 60°C (Poises) (ASTM D2170)							
Original	1911	3438	2000	1939	1517	1693	1835
TFOT	5431	10680	5347	4654	8737	5079	4642
RTFOT	5256	66330	7167	5708	5547	6202	9963
Viscosity Ratio at 60°C							
TFOT	2.84	3.11	2.67	2.40	5.76	3.00	2.53
RTFOT	2.75	19.20	3.58	2.94	3.65	3.66	5.43

(1) Test performed on the residue.

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11. FIGURES

Figure 1

VACUUM REDUCED ASPHALTS FROM COLD LAKE AND UPGRADED COLD LAKE

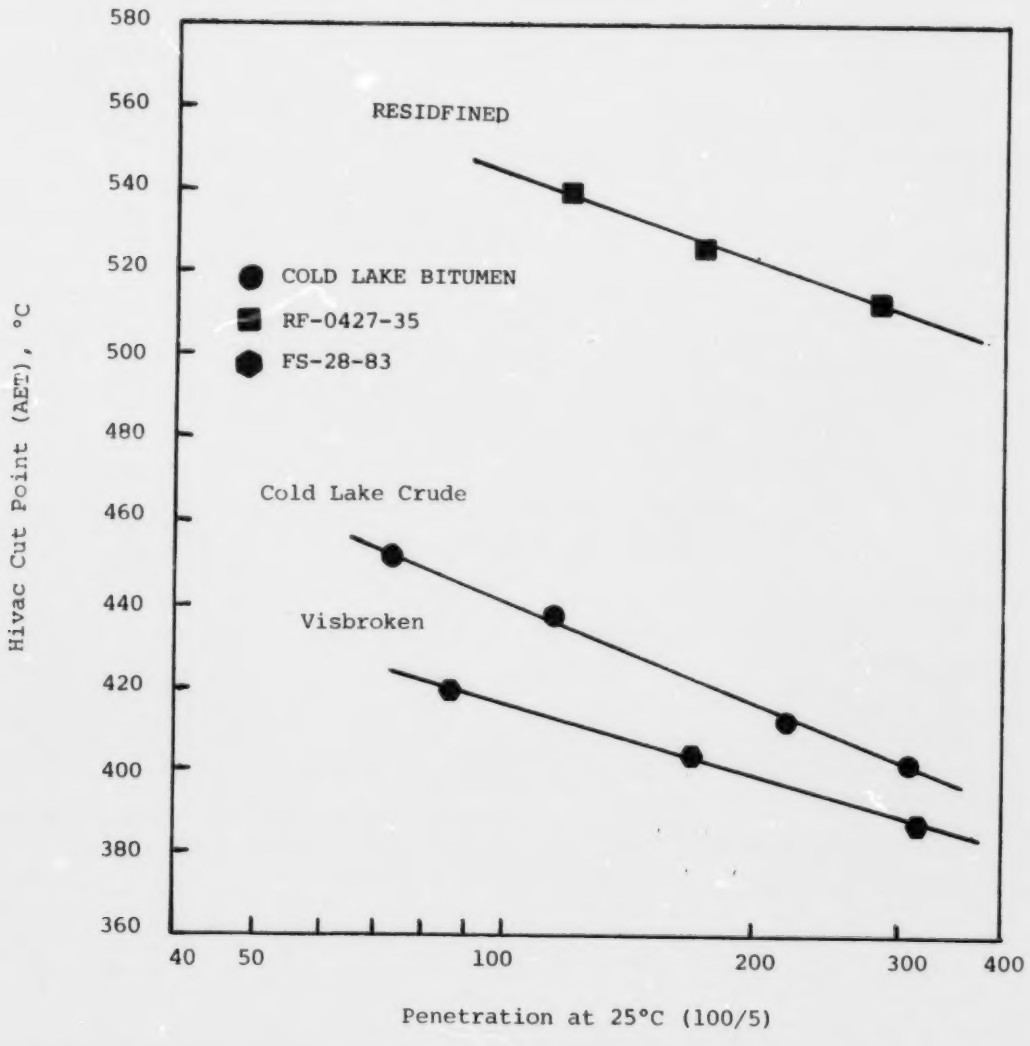


Figure 2

VACUUM REDUCED ASPHALTS FROM COLD LAKE
AND UPGRADED COLD LAKE

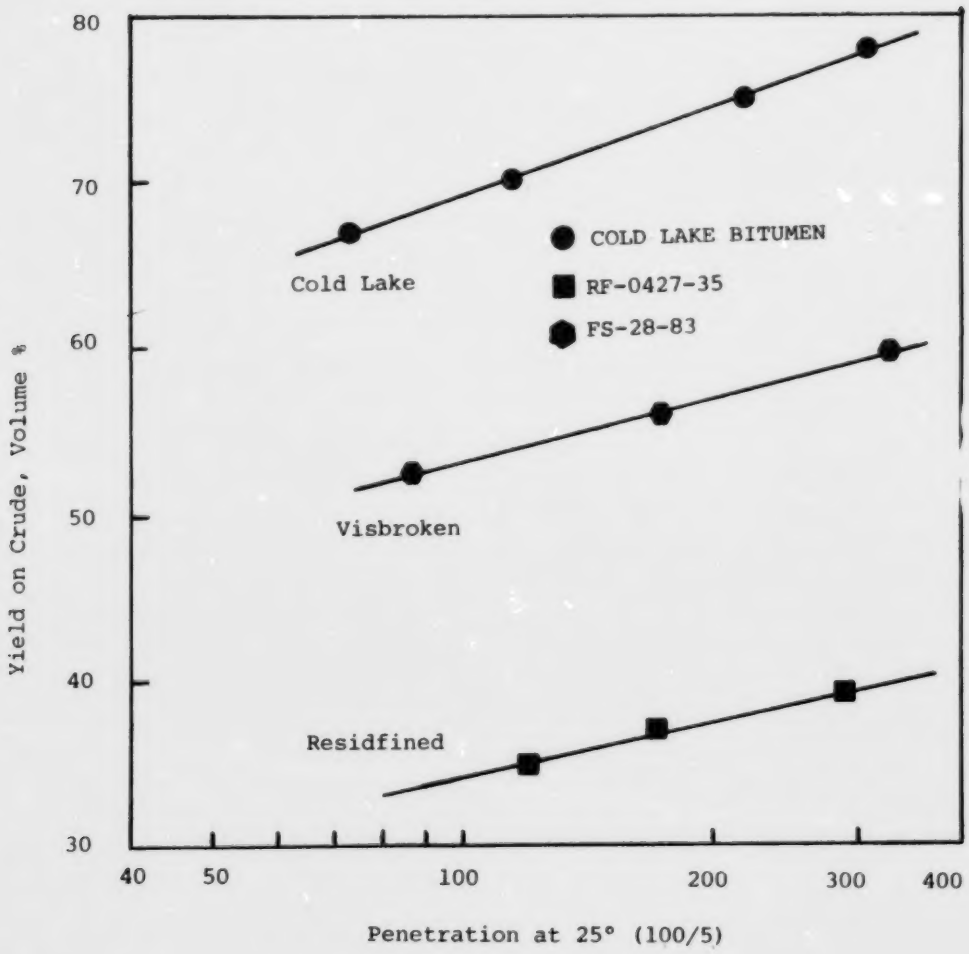


FIGURE 3

Viscosity of Conversion Residues and Blends with Cold Lake Vacuum Residue vs Ontario Specifications

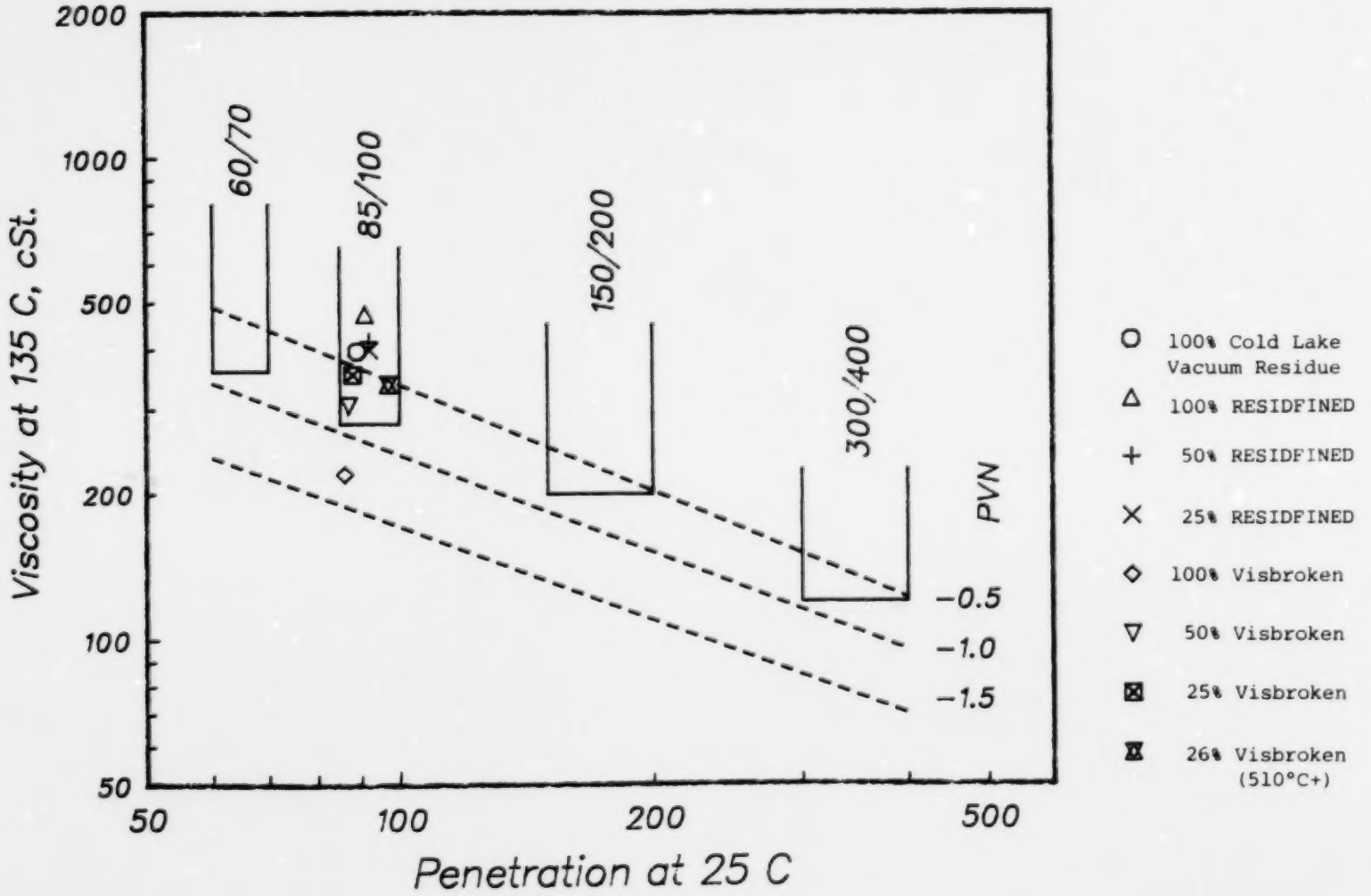


FIGURE 4

Viscosity of Conversion Residues and Blends with Cold Lake Vacuum Residue vs Alberta Specifications

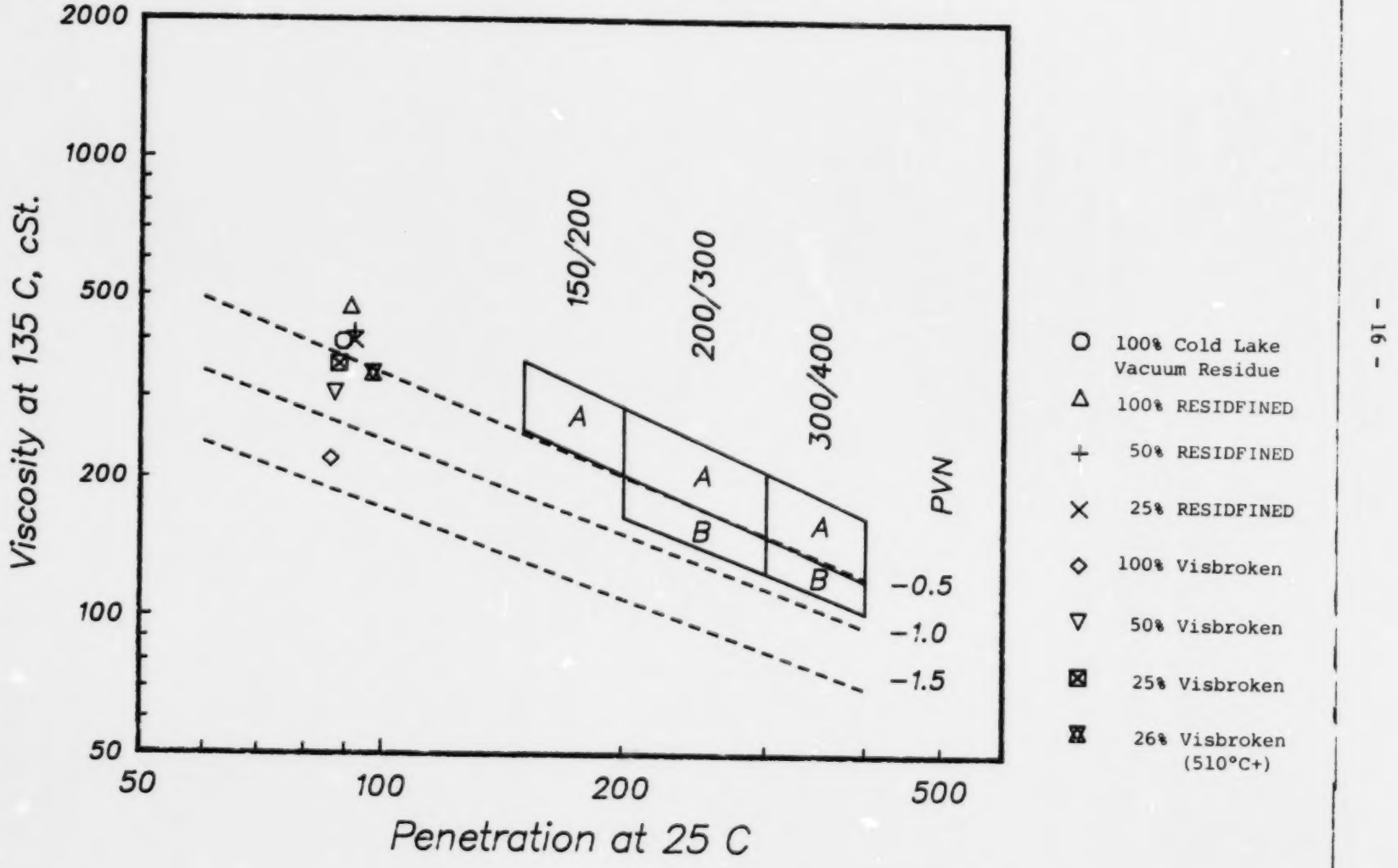


FIGURE 5

Viscosity of Conversion Residues and Blends with Cold Lake Vacuum Residue vs New Brunswick Specifications

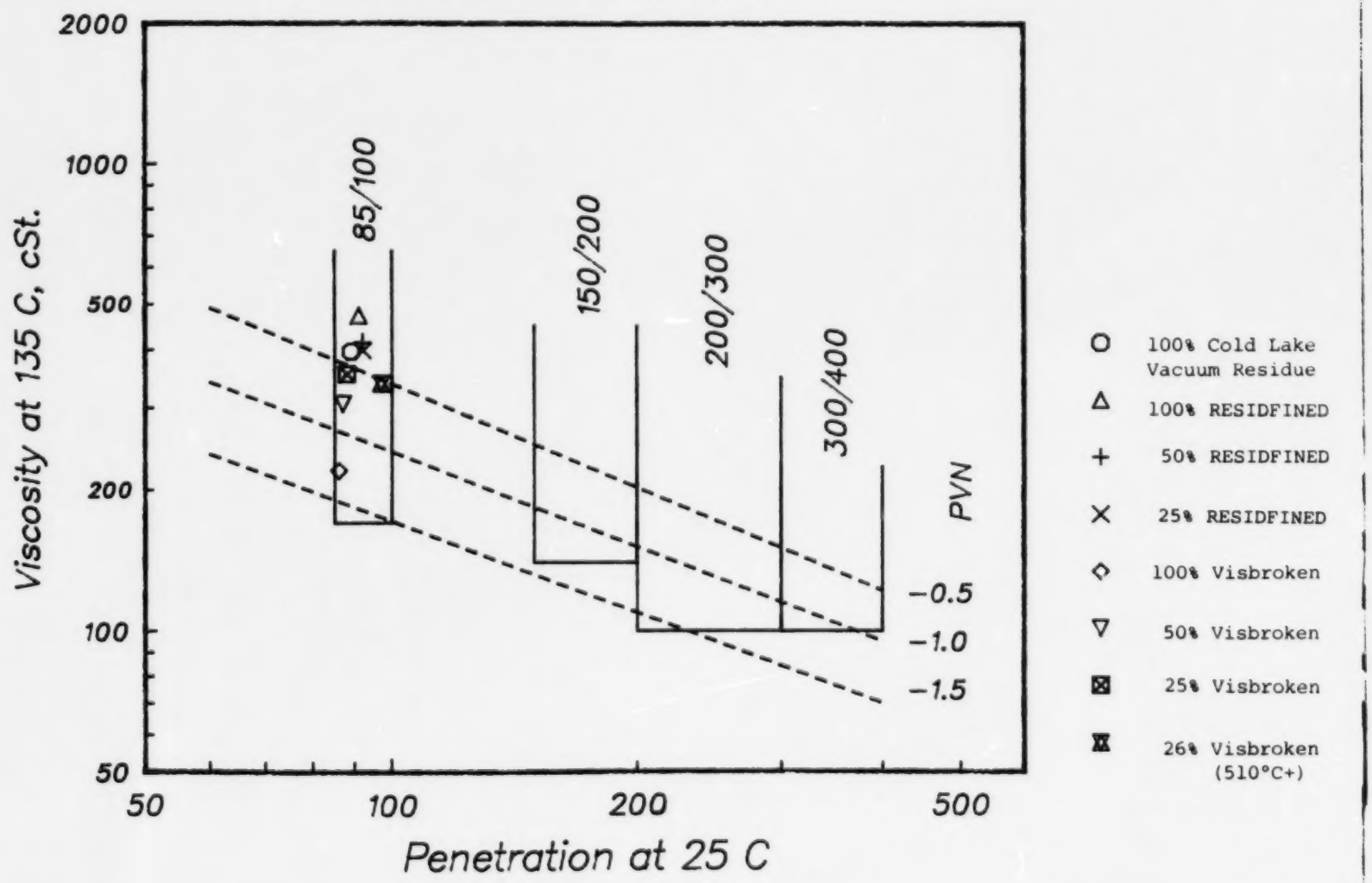


FIGURE 6

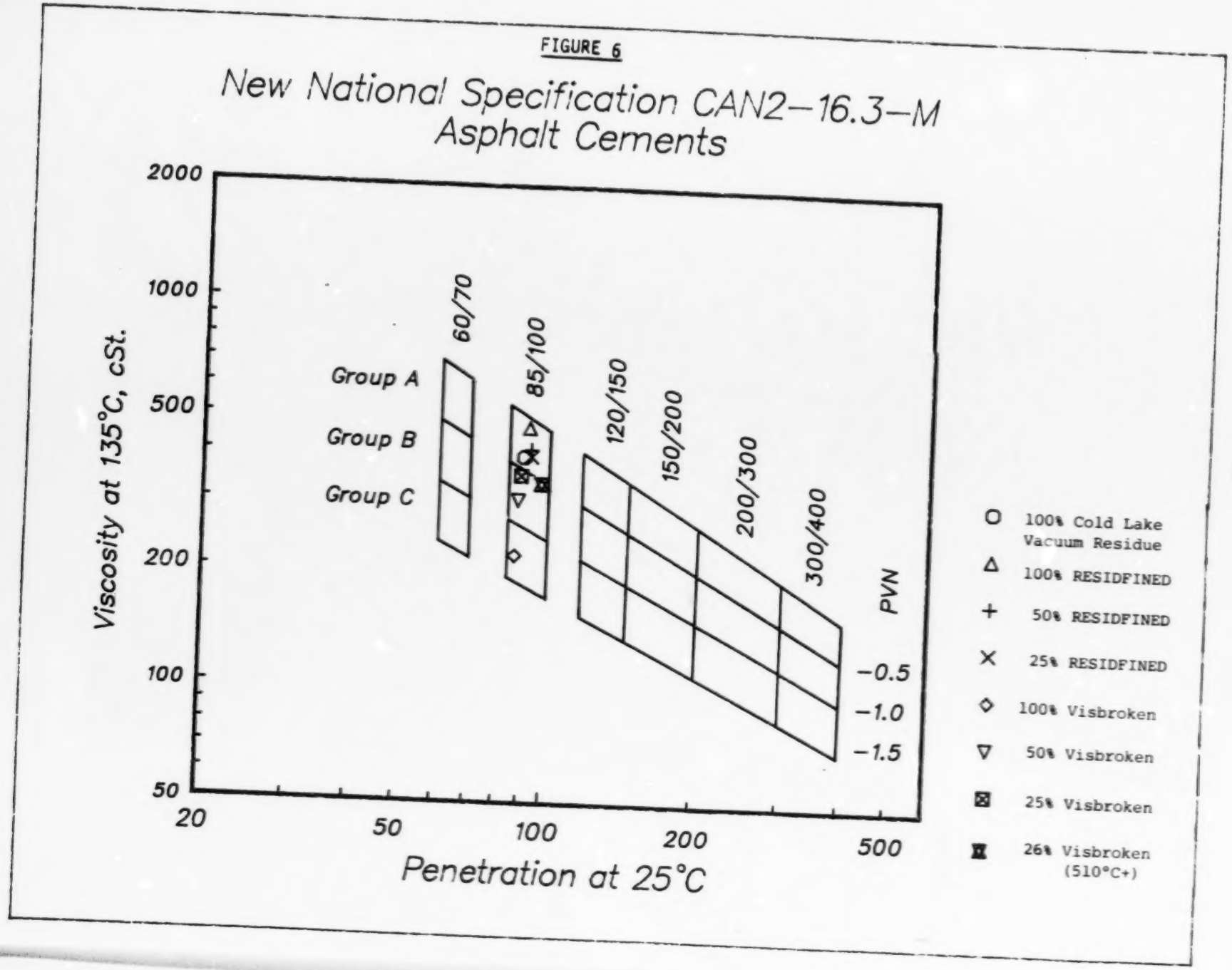

New National Specification CAN2-16.3-M
Asphalt Cements
Viscosity at 135°C, cSt.
2000
1000
500
200
100
50
20
50
100
200
500
Penetration at 25°C
Group A
Group B
Group C
60/70
85/100
120/150
150/200
200/300
300/400
PVN
-0.5
-1.0
-1.5
100% Cold Lake Vacuum Residue
100% RESIDFINED
50% RESIDFINED
25% RESIDFINED
100% Visbroken
50% Visbroken
25% Visbroken
26% Visbroken (510°C+)

FIGURE 7

COMPOUND-TYPE SEPARATION SCHEME
ASTM D4124

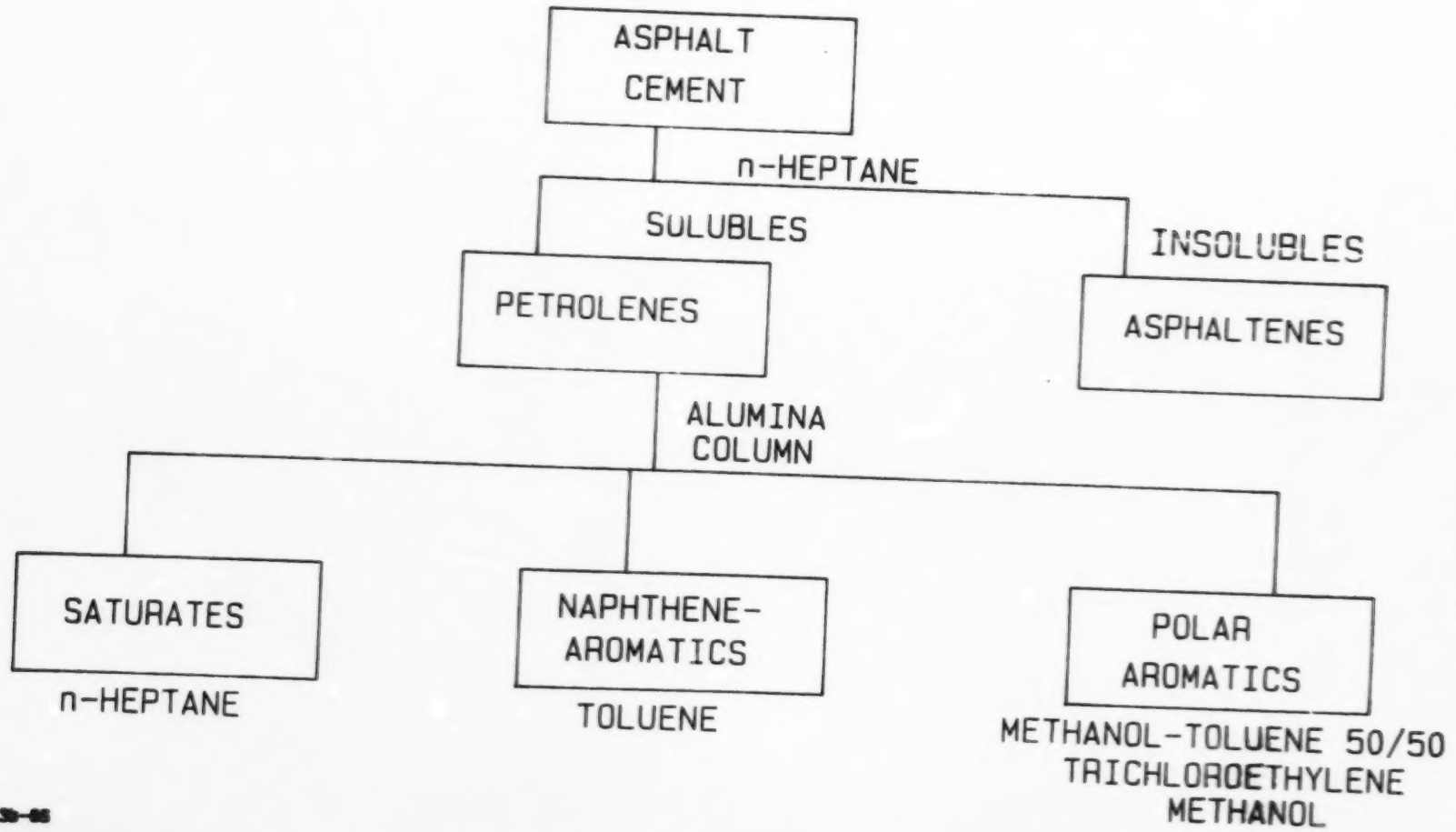


Figure 8

EFFECT OF AGING ON THE VISCOSITY OF 100% COLD LAKE VACUUM RESIDUE (SAMPLE 1)

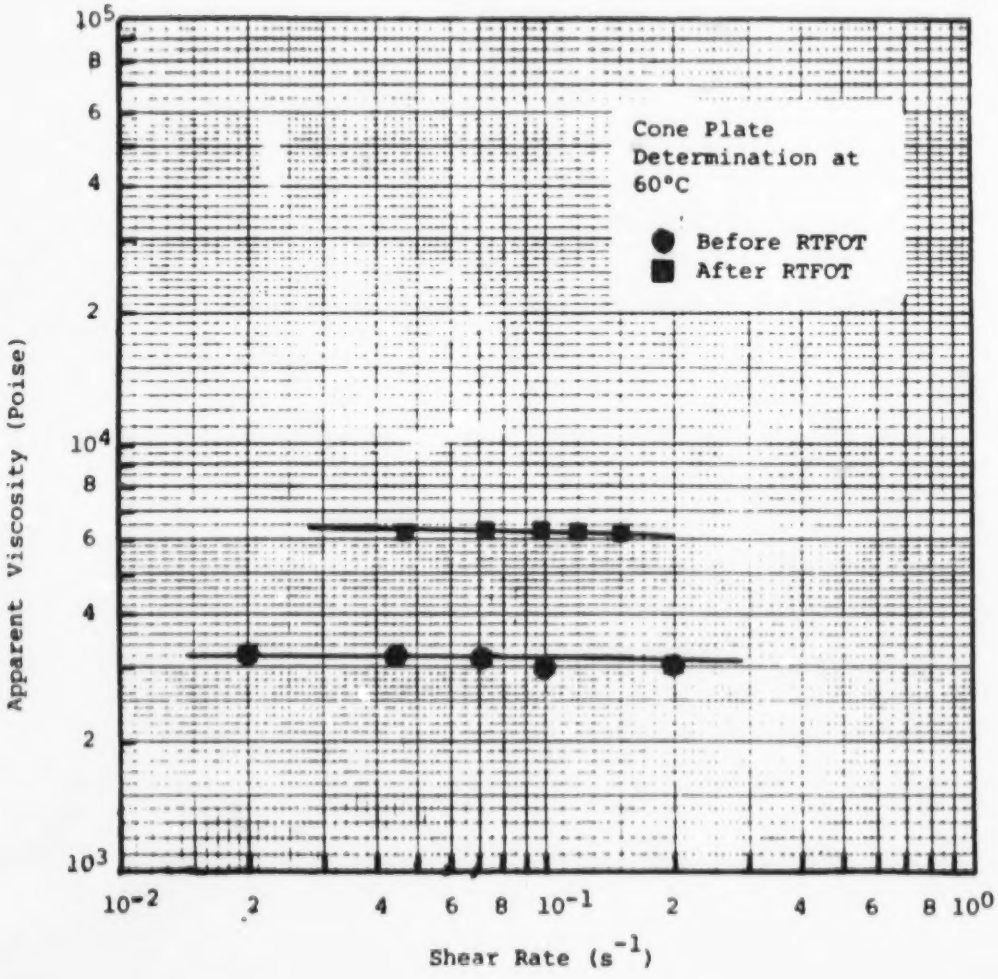


Figure 9

EFFECT OF AGING ON THE VISCOSITY OF 100% RESIDFINED RESIDUE

(SAMPLE 2)

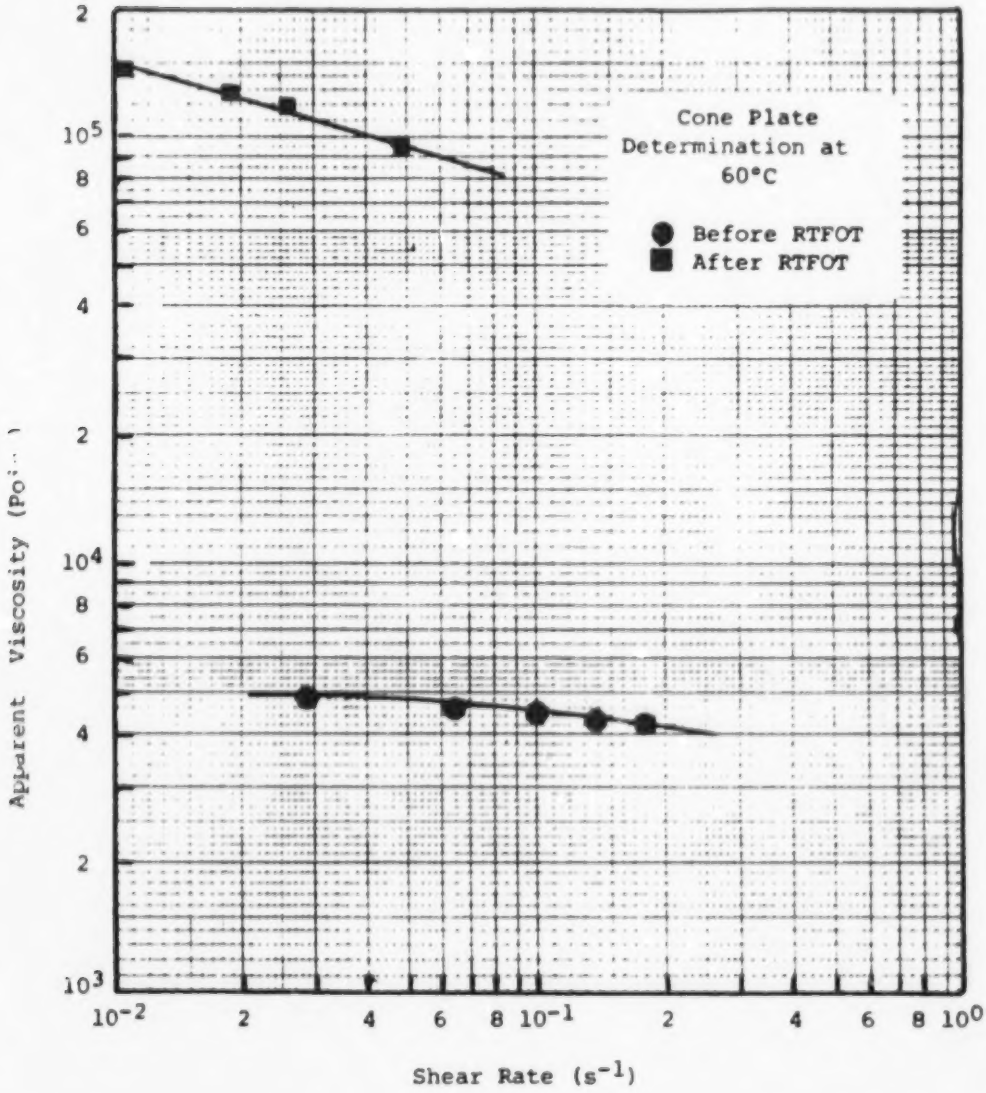


Figure 10

EFFECT OF AGING ON THE VISCOSITY OF 50 WT% RESIDFINED
50 WT% COLD LAKE VACUUM RESIDUE (SAMPLE 3)

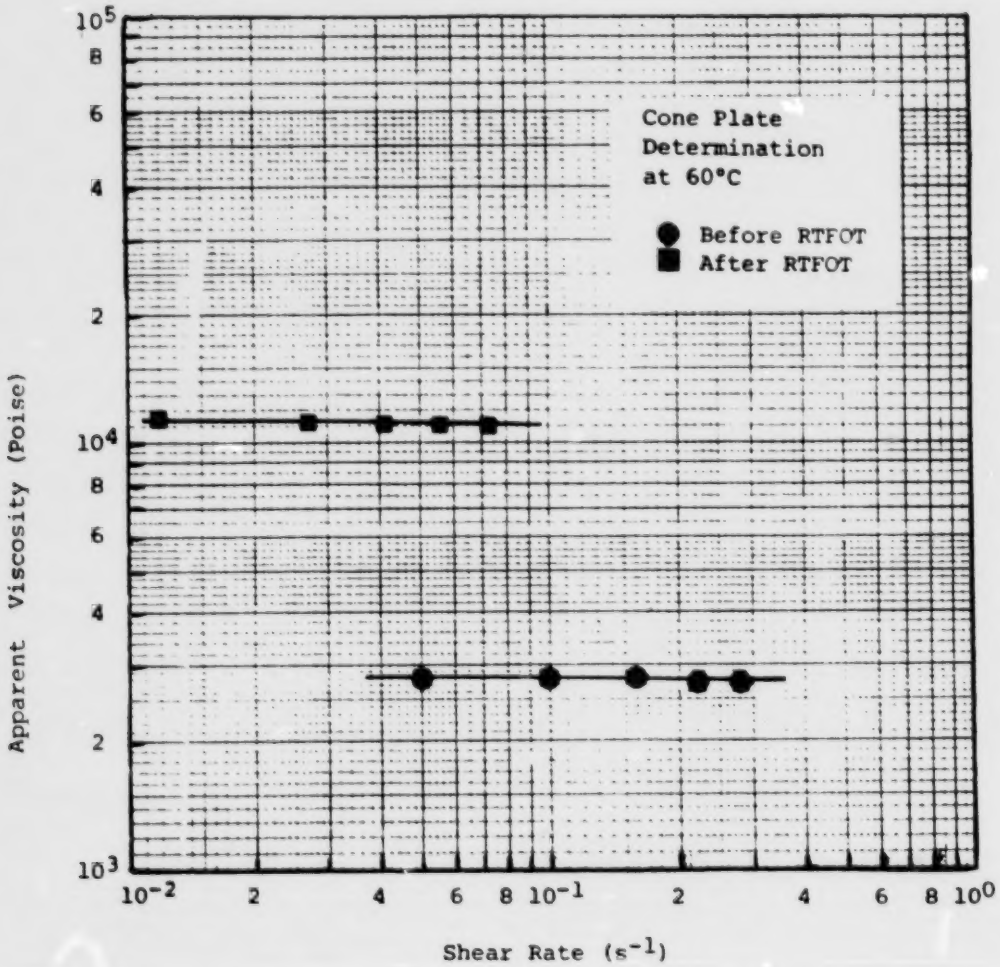


Figure 11

EFFECT OF AGING ON THE VISCOSITY OF 25 WT% RESIDFINED 75 WT% VACUUM REDUCED COLD LAKE RESIDUE (SAMPLE 4)

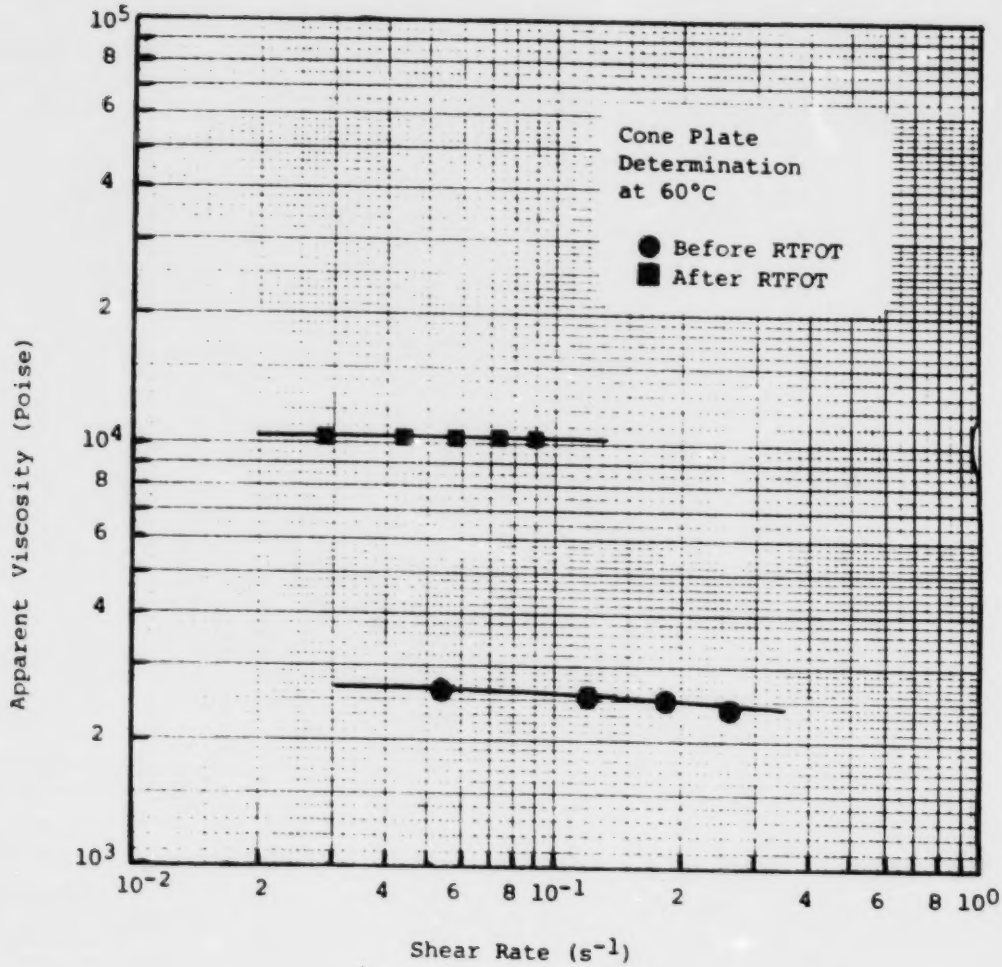


Figure 12

EFFECT OF AGING ON THE VISCOSITY OF 100% VISBROKEN RESIDUE

(SAMPLE 5)

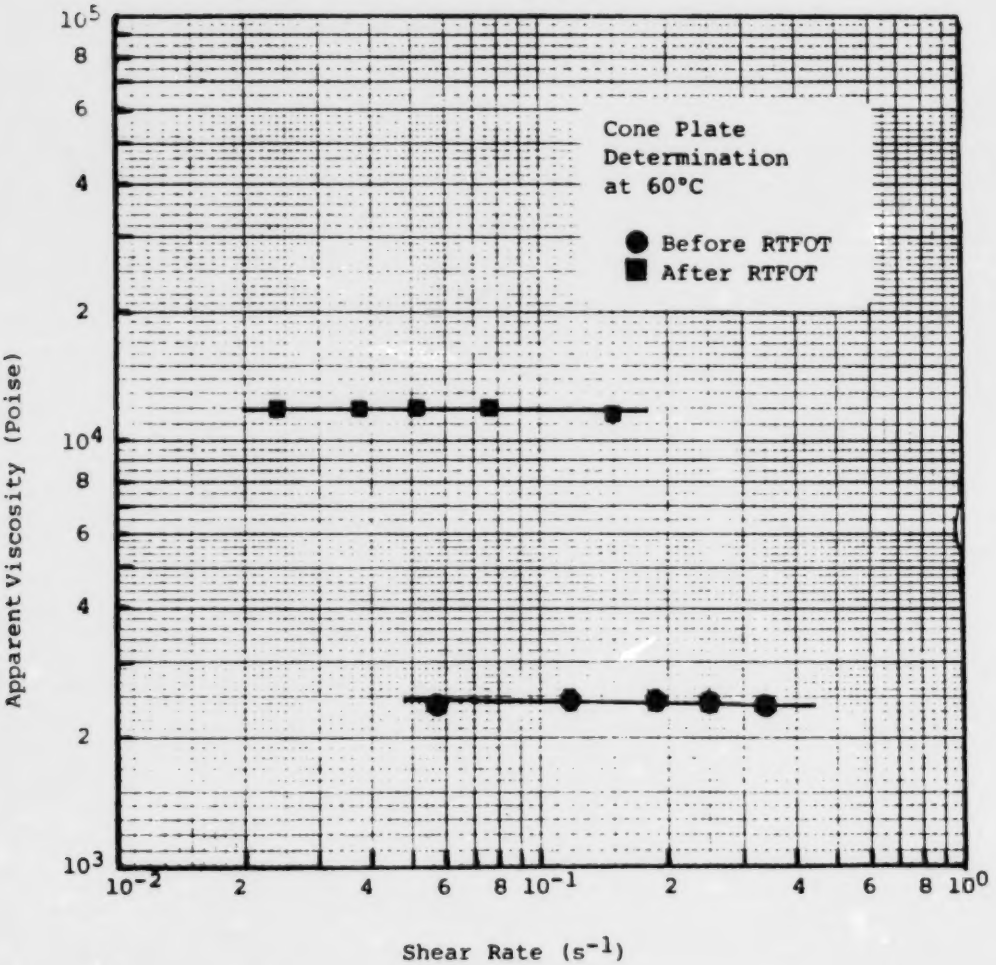


Figure 13

EFFECT OF AGING ON THE VISCOSITY OF 50 WT% VISBROKEN
50 WT% VACUUM REDUCED COLD LAKE RESIDUE (SAMPLE 6)

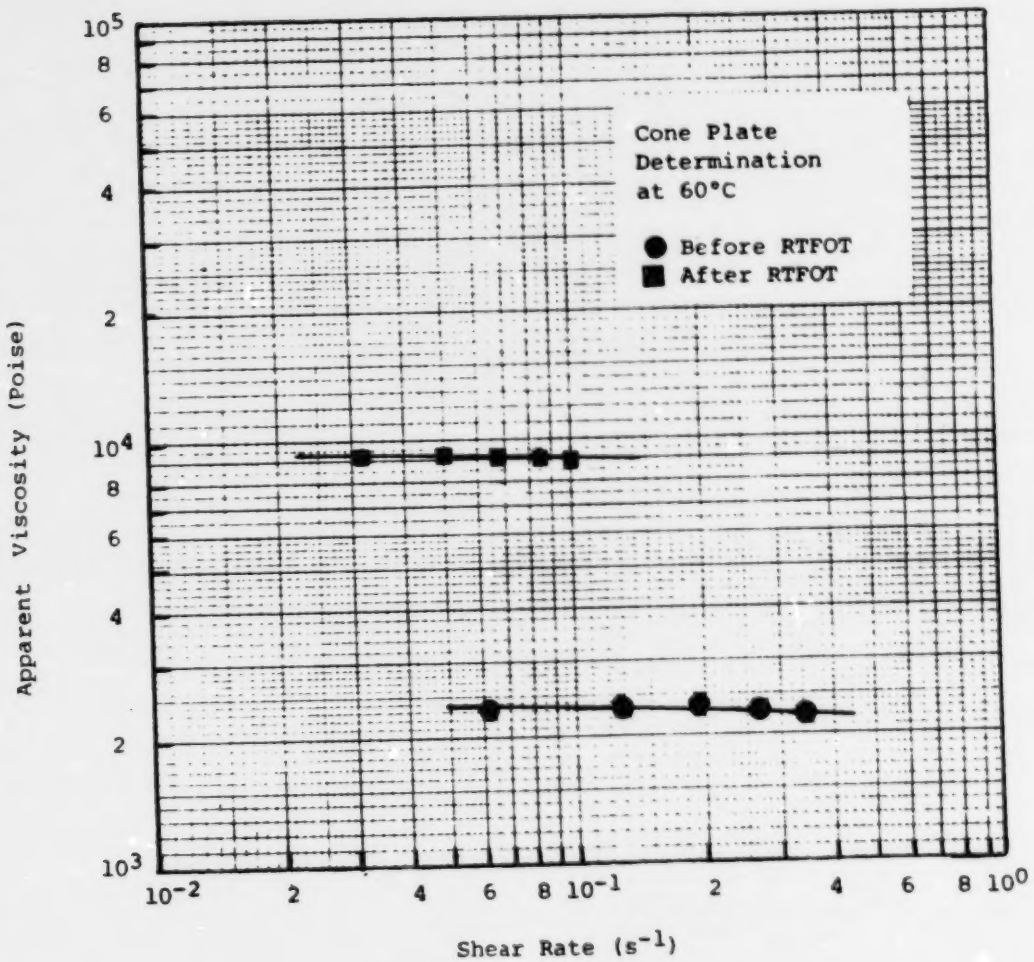
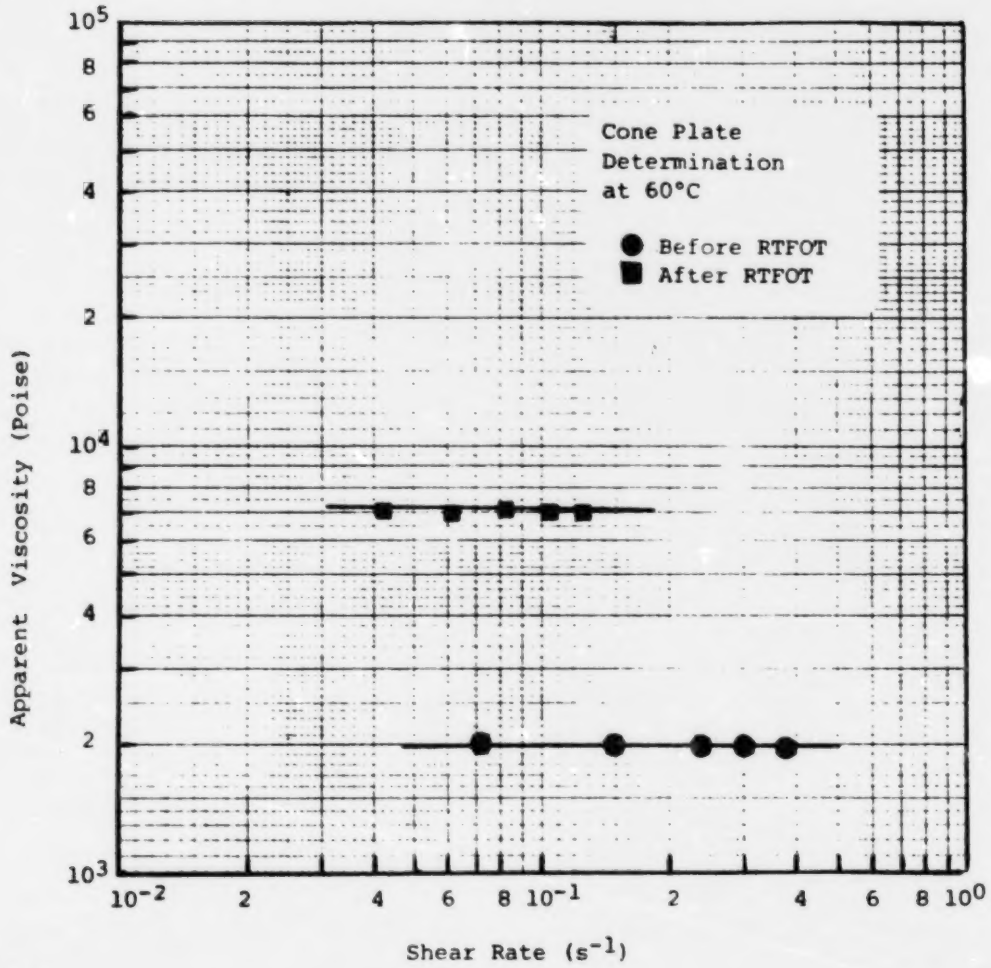


Figure 14

EFFECT OF AGING ON THE VISCOSITY OF 25 WT% VISBROKEN/
75 WT% VACUUM REDUCED COLD LAKE RESIDUE (SAMPLE 7)



QUALITY AND APPLICATIONS OF ASPHALT DERIVED FROM UPGRADED HEAVY CRUDE
PART 2. ROOFING ASPHALTS

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1. INTRODUCTION

Conventional roofing asphalt produced in refineries is obtained from catalytic or non-catalytic oxidation of distillation residues. With changing economics, the petroleum industry is now looking to upgrade heavy crude distillation residues to produce more transportation fuels. However, upgrading has a major impact on the quality of paving and roofing asphalt. In order to give good performance, roofing asphalt has to meet standard specifications for various uses.

It is well known that residues from conversion processes such as RESIDFINING and Visbreaking are not suitable for paving asphalt, as they don't meet specifications. In this study, evaluation of RESIDFINING and Cold Lake/RESIDFINING blends as roofing asphalt feedstock has been made.

The objective of this study is to obtain roofing asphalts made from conversion residues which are comparable to conventional air blown asphalts. Oxidation has been performed without a catalyst. Blending of upgraded residues into conventional asphalt would allow utilization of unconverted bottoms to produce good quality roofing asphalt, and alleviate a major problem of bottoms disposal. Presently, refineries having upgraders dispose of residual via combustion processes. Blending into asphalt represents a much more desirable economic outlet.

2. EXPERIMENTAL

Blending

RESIDFINING residue to be blended was prepared by distillation of the total RESIDFINER product to make a 300-400 penetration residue. The feedstock blend was prepared by mixing 50 wt% 300-400 penetration Cold Lake asphalt with 50 wt% of RESIDFINED 300-400 penetration asphalt. The yield and cut point for the 300-400 penetration asphalts as well as the characteristics of the oxidation feedstock are presented in Table 1.

Oxidation

The feedstock was oxidized without catalyst to the desired softening point at 260°C using 50 l/h/kg air flow rate in a laboratory oxidizer. Progression of the oxidation was followed by determining the softening point at different reaction times. The oxidation curves are shown in Figure 1.

Analysis

The following tests on roofing asphalt were performed according to ASTM procedures.

(a)	Softening Point, °C	ASTM D36
(b)	Penetration, 0°C, 200 g, 60 s 25°C, 100 g, 5 s 45°C, 100 g, 5 s	ASTM D5
(c)	Solubility in trichloroethylene, %	ASTM D2042
(d)	Compound-type distribution	ASTM D4124

RESULTS AND DISCUSSION

3. PROPERTIES OF THE ASPHALTS

The Canadian Standards Association Requirement properties for built-up roof mopping asphalts are shown in Table 2.

The physical properties of oxidized Cold Lake vacuum residue, RESIDFINING, and Cold Lake/RESIDFINING 50/50, roofing asphalts are presented in Table 3. Examination of the results show that oxidation of Cold Lake 300/400 asphalt allows preparation of Type 1, Type 2 and Type 3 roofing asphalts although penetration of Type 2 and Type 3 asphalts is at the lower end of the specification range. However, roofing asphalts obtained by oxidation of RESIDFINING 300/400 pen does not meet the specifications. For a given softening point, the penetration is far too high. Consequently, the penetration at various temperatures (0, 25, 45°C) do not fall within the penetration range required in the specifications.

The oxidation of a Cold Lake/RESIDFINING 50/50 blend produces Type 1 and Type 3 roofing asphalt that meet specifications. One of the products does not meet Type 2 roofing asphalt because the penetration at 25°C is a little bit too high. The results are illustrated in Figure 2. The figure shows that a much better product could be obtained by blending between 20 to 40 wt% of RESIDFINING 300/400 pen into Cold Lake 300/400 pen prior to the oxidation. However, blend optimization was not investigated in this study.

Another interesting point to be mentioned is that under the experimental conditions used in this study, oxidation of RESIDFINING 300/400 pen does not produce coke as shown by its solubility in trichloroethylene.

4. COMPOUND-TYPE DISTRIBUTION

The composition of asphalts has been recognized for a long time as an important factor in controlling the performance of such materials(1,2). Although performance has not been investigated in this work, it was interesting to see how the oxidation affects the composition of upgraded asphalts.

The roofing asphalts prepared in this work have been deasphalted with n-heptane followed by separation of the n-heptane soluble portion into saturates, naphthene-aromatics and polar aromatics according to the ASTM D 4124 procedure. The schematic of the separation is illustrated in Figure 3. The compound-type distribution results are presented in Table 4.

The effect of the oxidation on the compound-type distribution is illustrated in Figures 4 to 6. The results show that the saturates content is not affected by the oxidation. The same trend is observed for asphalts from Cold Lake, crude residue, the RESIDFINING, process and the blended asphalt. However, examination of the naphthene-aromatics content shows an average decrease of 14.7% for all the asphalts.

RESIDFINING residues have higher saturates naphthene-aromatics contents and lower polar aromatics asphaltenes contents compared to Cold Lake vacuum residue. The saturates and naphthene-aromatics are usually liquid in nature whereas the polar aromatics and asphaltenes are solid. This difference in composition accounts for the higher penetration values found for asphalts containing RESIDFINING residue (Figure 2).

The polar aromatics are more significantly affected by the oxidation than the naphthene-aromatics. The data indicate an average drop of the polar aromatics content of about 24.4% for these asphalts. This drop seems to level off with further oxidation. It would appear that as much polar aromatics are formed from the naphthene-aromatics as asphaltenes from the polar aromatics beyond a certain oxidation period. In summary, the following trend is observed:

$$\text{NAPHTHENE-AROMATICS} \xrightarrow{[O]} \text{POLAR AROMATICS} \xrightarrow{[O]} \text{ASPHALTENES}$$

The naphthene-aromatics are oxidized to polar aromatics and the latter to asphaltenes. Association of polar aromatic components through hydrogen and formation of C-C bonds leads to asphaltenes. As a result, the asphaltenes content increases by an average of 48.4% by the end of the oxidation. Increasing of asphaltenes content leads to increasing the softening point and decreasing penetration of asphalt. Net result of oxidation is conversion of both naphthene-aromatics and polar aromatics to asphaltenes.

5. CONCLUSIONS

This study has shown that 100% 300/400 pen RESIDFINING Cold Lake bottom is suitable as oxidation feedstock for the production of roof mopping asphalts, but would require readjustment of the feedstock viscosity to meet the specifications. However, blending of RESIDFINING 300/400 pen with Cold Lake 300/400 pen (50 wt% blend) asphalts produce an acceptable feedstock for roofing asphalts. The results indicate that better mopping asphalts would be obtained by blending between 20 to 40 wt% of RESIDFINING 300/400 pen with Cold Lake 300/400 pen asphalts. Differences in the naphthene-aromatics/polar aromatics ratio accounts for the major difference in the properties of roof mopping asphalts made using RESIDFINING residue.

6. REFERENCES

1. L.W. Corbett, "Relationship Between Composition and Physical Properties of Asphalt", Proceedings of the AAPT, 39, 481 (1970).

2. L.W. Corbett and H.E. Schweyer, "Composition of Rheology Considerations in Age Hardening of Bitumen", Proceedings of the AAPT, 50, 571 (1981).

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Attachments
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7. TABLES

TABLE 1

OXIDATION FEEDSTOCK CHARACTERISTICS (300-400 PEN)

	Cold Lake	RESIDFINED	50 wt% Cold Lake 50 wt% RESIDFINED
Cut Point, °C	404	506	-
Yield on Crude, vol%	-	41.0	-
Viscosity at 100°C, cSt	1027	1040	1049
Softening Point, °C	32.7	32.8	32.8
Penetration at 25°C (100/5)	315	325	321
Flash Point, °C	264	330	272

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TABLE 2

ASPHALT REQUIREMENTS FOR ROOFING PURPOSES

Property	Type 1		Type 2		Type 3	
	Min.	Max.	Min.	Max.	Min.	Max.
Softening Point, R&B, °C	60	68	75	83	90	98
Flash Point, COC, °C	230	-	230	-	230	-
Penetration						
0°C, 200 g, 60 s	10	-	10	-	8	-
25°C, 100 g, 5 s	30	45	20	30	15	25
45°C, 50 g, 5 s	-	160	-	80	-	55
Loss on Heating, %	-	1.0	-	1.0	-	1.0
% of Original	80	-	80	-	80	-
Solubility in Trichloroethylene, %	99	-	99	-	99	-

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TABLE 3

PROPERTIES OF THE AIR BLOWN ASPHALTS

Property	Type 1	Type 2	Type 3
Cold Lake 300-400 Pen			
Softening Point, °C (D36)	65	77	95
Penetration			
0°C, 200 g, 60 s	15	12	9
25°C, 100 g, 5 s	32	21	15
45°C, 50 g, 5 s	85	47	28
Solubility in Trichloroethylene, %	99.99	99.99	99.98
RESIDFINING, 300-400 Pen (RF 04 27)			
Softening Point, °C (D36)	67	77	95
Penetration			
0°C, 200 g, 60 s	38	34	28
25°C, 100 g, 5 s	68	53	42
45°C, 50 g, 5 s	121	81	59
Solubility in Trichloroethylene, %	99.98	99.97	99.97
Cold Lake, 300-400 Pen (50 wt%) RESIDFINING, 300-400 Pen (50 wt%)			
Softening Point, °C (D36)	66	78	96
Penetration			
0°C, 200 g, 60 s	24	18	16
25°C, 100 g, 5 s	43	31	24
45°C, 50 g, 5 s	94	56	33
Solubility in Trichloroethylene, %	99.98	99.92	99.85

TABLE 4

COMPOUND-TYPE DISTRIBUTION OF ORIGINAL AND AIR BLOWN ASPHALTS, WT%

ASTM D 4124

	Saturates	Naphthene-Aromatics	Polar Aromatics	Asphaltenes
Feedstock: Cold Lake 300/400 Pen Residue				
Original	14.0	33.8	36.1	16.1
(a)Type 1	13.1	32.0	26.5	28.4
(b)Type 2	12.8	31.0	24.8	31.4
(c)Type 3	12.4	28.3	25.6	33.7
Feedstock: RESIDFINING 300/400 Pen				
Original	16.5	45.5	23.6	14.4
Type 1	15.2	42.1	20.5	22.2
Type 2	15.9	39.7	20.6	23.8
Type 3	15.8	40.0	18.8	25.4
Feedstock: Cold Lake Residue/RESIDFINING 50/50				
Original	15.0	37.8	32.3	14.9
Type 1	15.2	34.7	24.2	25.9
Type 2	14.4	35.7	22.0	27.9
Type 3	14.0	31.8	24.6	29.6

(a) Type 1; S.P. = 60-68°C
(b) Type 2; S.P. = 75-83°C
(c) Type 3; S.P. = 90-98°C

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8. FIGURES

FIGURE 1

OXIDATION OF COLD LAKE VACUUM RESIDUE, RESIDFINING RESIDUE AND BLENDED ASPHALT

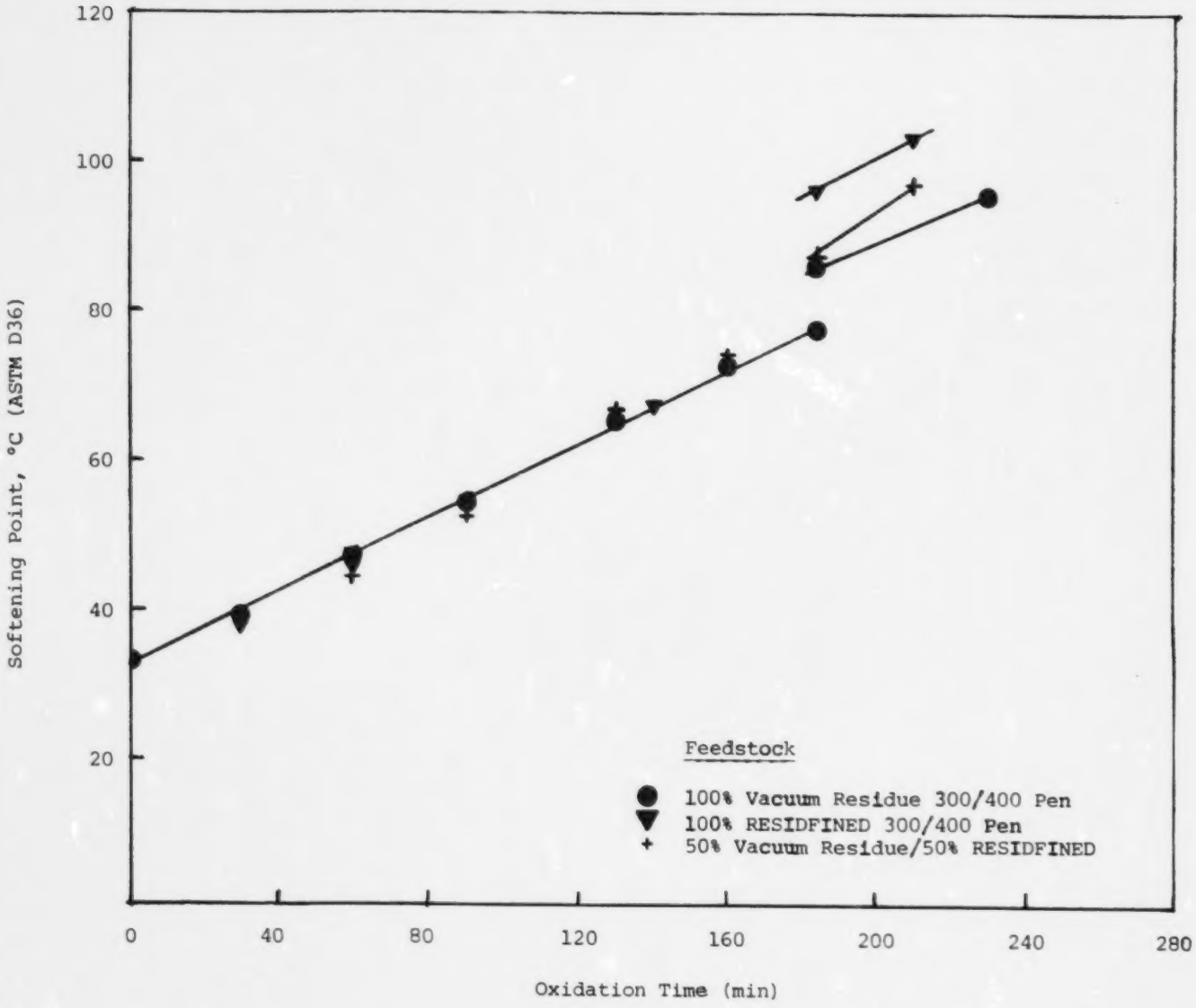

FIGURE 2

CANADIAN STANDARDS ASSOCIATION REQUIREMENTS
PROPERTIES OF BUILT-UP ROOF MOPPING ASPHALTS

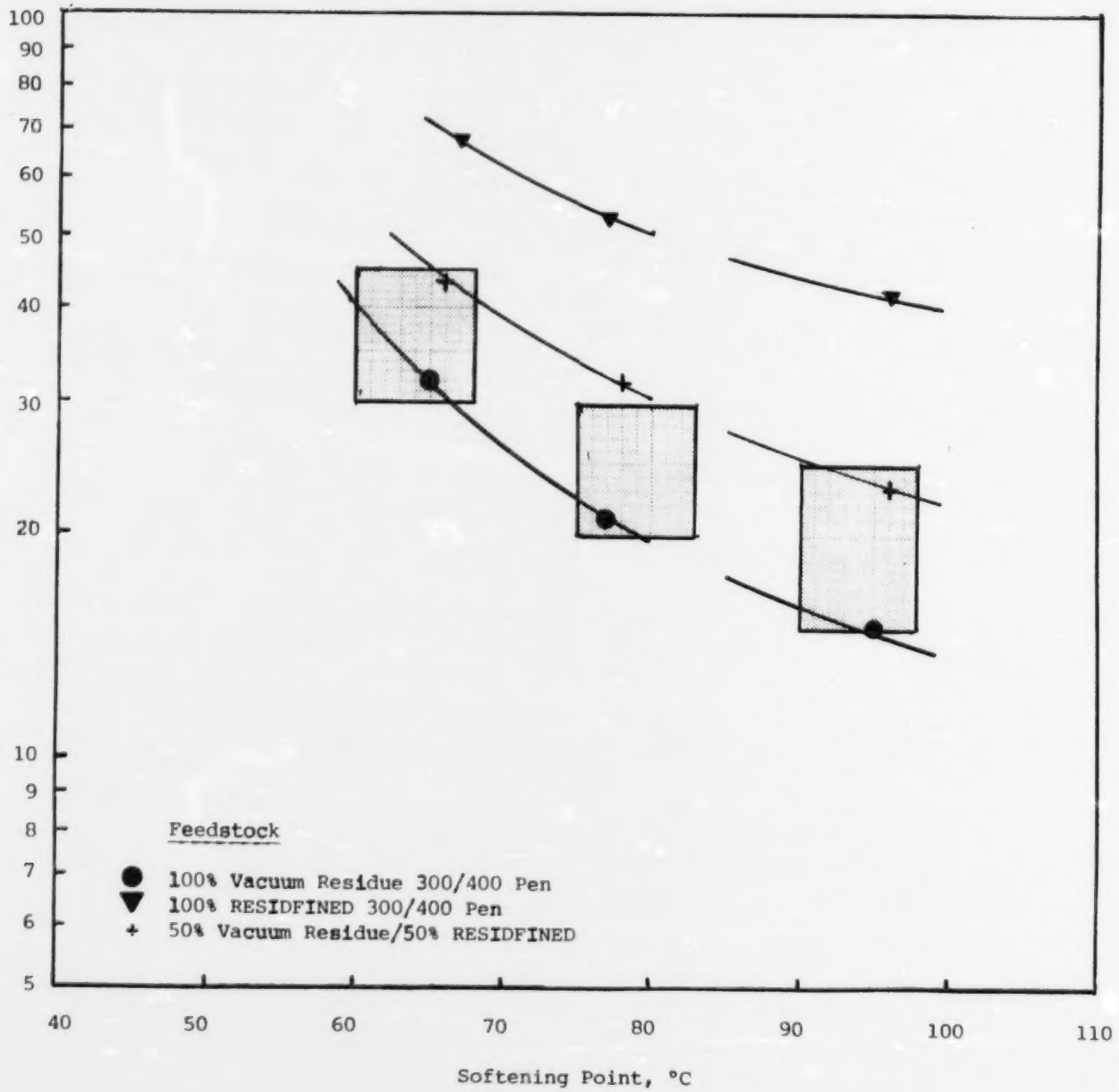

FIGURE 3

COMPOUND-TYPE SEPARATION SCHEME

ASTM D4124

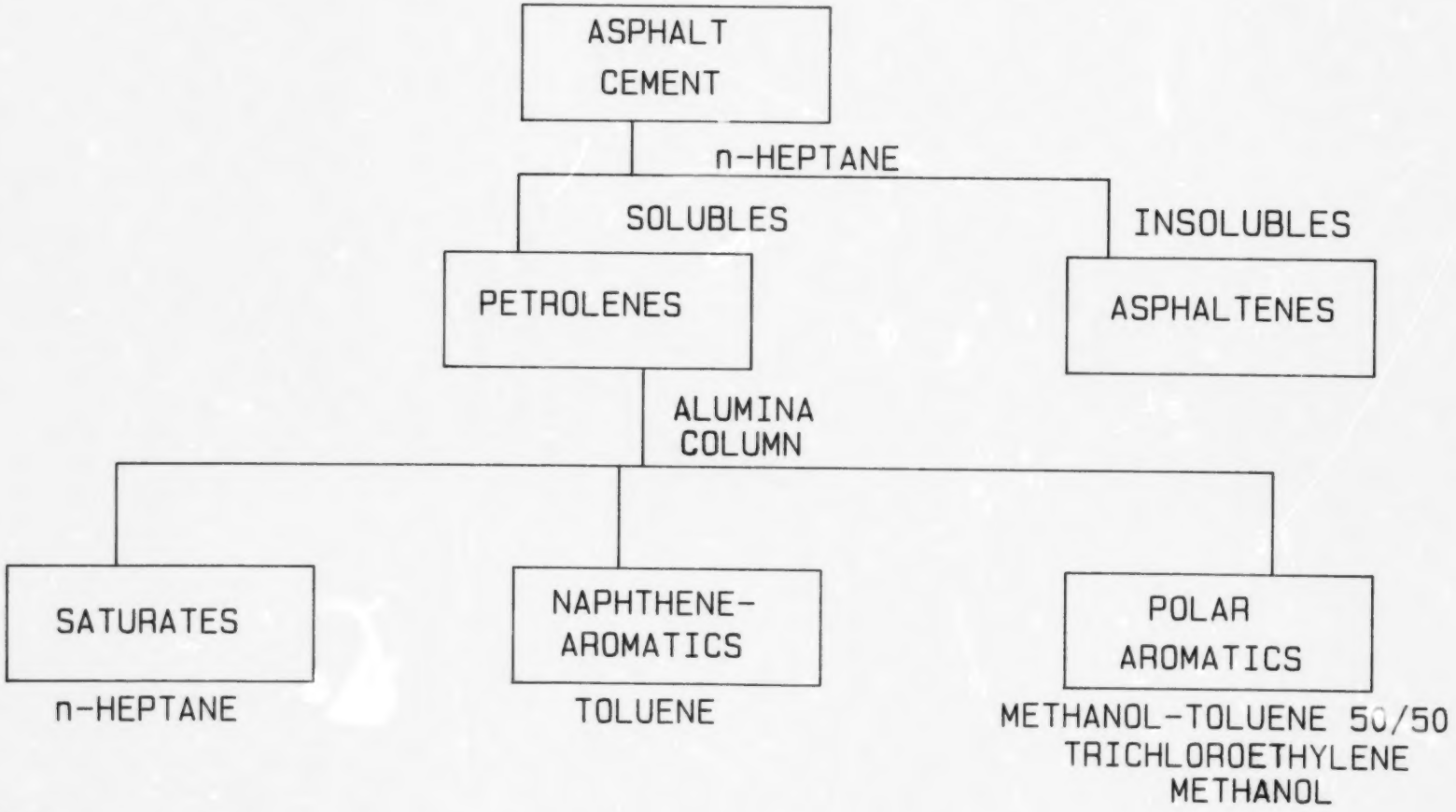

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FIGURE 4

EFFECT OF OXIDATION ON THE COMPOSITION OF
100% VACUUM RESIDUE, WT% (COLD LAKE 300/400 PEN)

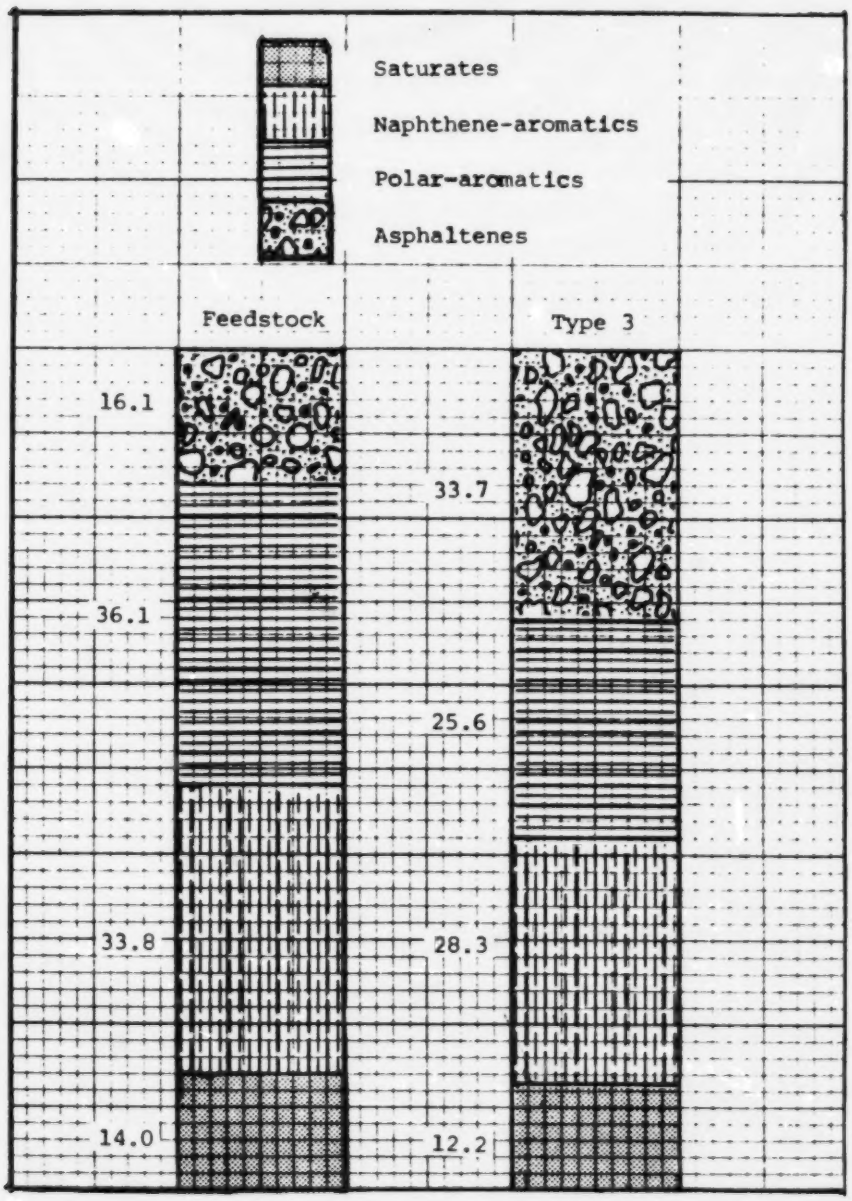

FIGURE 5

EFFECT OF OXIDATION ON THE COMPOSITION OF
100% RESIDFINED RESIDUE, WT%

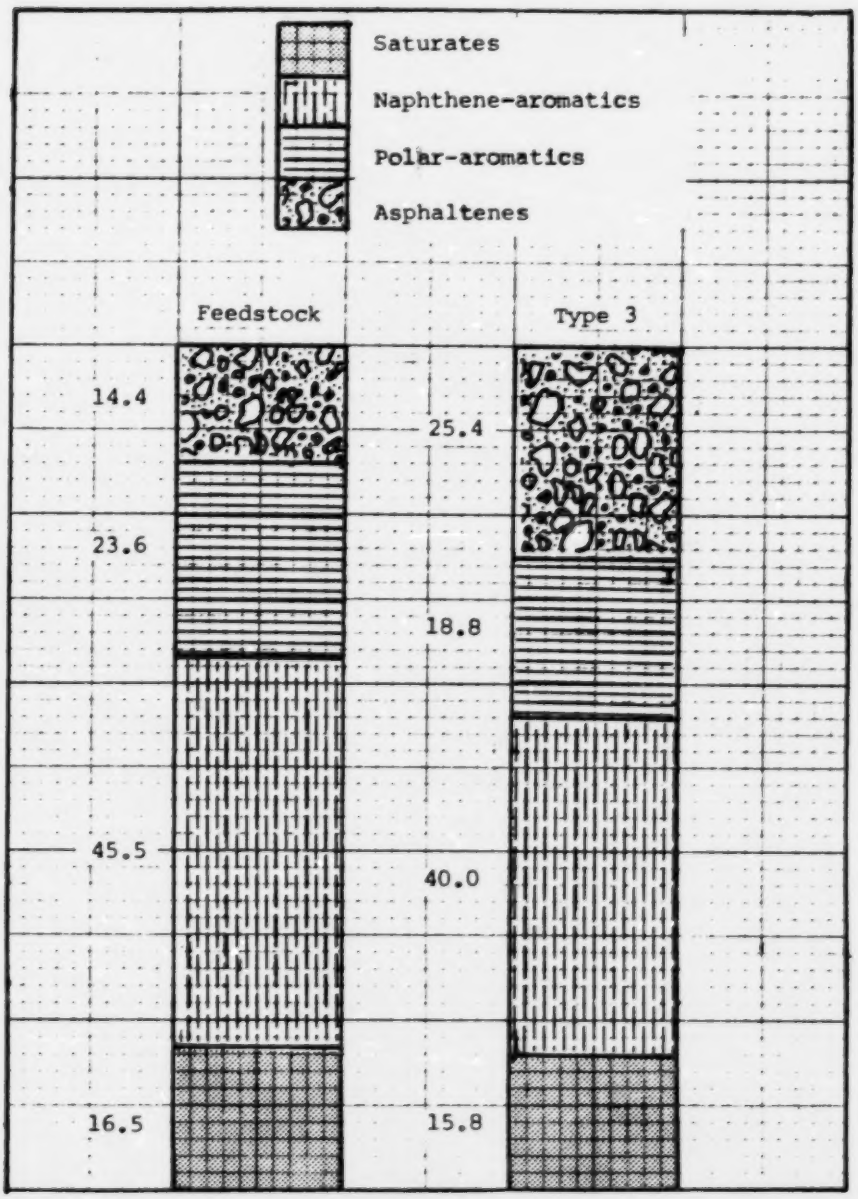

FIGURE 6

EFFECT OF OXIDATION ON THE COMPOSITION OF
50% VACUUM RESIDUE/50% RESIDFINED RESIDUE, WT%